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IN NEUTRAL CORROSIVE MEDIA

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ON THE ROLE OF HYDROGEN IN THE PROCESS OF STEEL FAILURE
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ABSTRACT. Low-cycle plastic fatigue (alternating deformation above the yield point) was studied on 08 KP steel (0.09% C, 0.37% Mn, 0.019% Si, traces of P and S) in order to determine low degrees of hydrogen absorption taking place in neutral electrolytes (3% NaCl solution). The specimens were subjected to bend tests beyond the elastic limits (plastic fatigue) at a frequency of 0.8 cps on an IMA IP-1 machine. A platinum spiral served as the anode during polarization. From the test results, "polarization curves," *i.e.*, graphs of plastic fatigue (number of cycles up to failure) versus density of the cathodic polarization current were plotted. The curves obtained for the action of neutral and acid electrolytes in the presence of cathodic polarization were qualitatively similar, which constitutes an indirect confirmation of the hydrogen embrittlement of the metal in neutral electrolytes in the presence of plastic fatigue. The decrease in plastic fatigue under the influence of hydrogen at relatively low cathodic current densities is reinforced by the presence of stress concentrators produced by selective corrosion.

Side by side with the opinion that carbon steels may absorb hydrogen in neutral electrolytes with $\text{pH} \approx 7$ [1-7], there exist other views which deny or neglect the effect of hydrogen on the mechanical properties of metals during corrosion-fatigue failure in these electrolytes [8-13]. /688*

The role of hydrogen in the failure process under these conditions can be determined by investigating the dependence of the mechanical properties on polarization current density, and by comparing the character of this dependence for neutral electrolytes with that observed in acid media in which hydrogen absorption unquestionably occurs.

In a number of studies [1, 2, 8-10, 12-14] it has been shown that in neutral electrolytes without any polarization current, corrosion-fatigue failure occurs as a result of the combined effect of mechanical stresses and electrochemical corrosion of the most active parts of the metal. In [2, 4] it was established that there exist critical cathode current densities above which there appears a pronounced tendency to cracking due to hydrogen absorption of the metal in neutral electrolytes. However, in other studies this was not observed. According to [8-12], a cathode current density greater than $5-10 \text{ A/dm}^2$ restores the mechanical properties of the metal to the level obtained in tests in air. The value of this density depends directly on the stresses, the acidity of the

*Numbers in the margin indicate pagination in the foreign text.

medium, and the ambient temperature. The authors feel that the restoration of the properties of the metal is due to the total neutralization of the effect of the corrosion factor by cathode protection.

However, in studies by other investigators [1, 2, 4, 6, 14], full restoration of mechanical properties under conditions of cathode protection was not observed. This may be due to intensification of the hydrogen absorption process which decreases the strength of steel at high cathode current densities.

Therefore, the problem of the effect of cathode polarization and of hydrogen on the corrosion fatigue strength of steel in neutral electrolytes at large cathode current densities (above 5-10 A/dm²) remains unsolved. Clarification of this problem must include an account of the role of stresses and strains, since the data in [1, 15-17] indicate that these factors significantly enhance the action of hydrogen on the mechanical properties of metals.

It should be noted that the critical values for cathode current densities observed in [2, 4] cannot be regarded a boundary between cathode and anode processes, but only as a limit between predominance of one or the other process. The conditions which determine the degree to which each of them participates in corrosion-fatigue destruction have not yet been investigated and require clarification. It is the purpose of this paper to resolve these problems.

Research Method

As is well known [18], the most sensitive method for detecting the effect of hydrogen on the properties of a metal is to subject specimens to mechanical plastic deformation tests such as alternate bending or torsion, in which even extremely small quantities of absorbed hydrogen interfere with plastic deformation and lead to rapid failure. Under these conditions local hydrogen concentration may attain very high values, although the average for the whole sample is insignificant.

The present paper contains a study of low-cycle plastic fatigue (alternating cyclic deformation above the yield point), which permitted estimation of small degrees of hydrogen absorption occurring in neutral electrolytes.

The investigations were made in flat specimens of 08 KP steel (0.09% C; 0.37% Mn; 0.019% Si; traces of P and S). The specimens (total length, 110 mm; length of the test section, 20 mm; cross section, 3 × 10 mm) were cut from a sheet in the direction of rolling, milled, annealed at 850°C, and then polished. Before testing, the specimens were carefully degreased with acetone and ethylene dichloride.

The corrosive medium was a 3% NaCl solution, chemically pure or with sulfuric acid added. During the test the electrolyte was agitated intensively and continuously renewed so that the solution was completely replaced every 30 minutes.

The specimens were subjected to two-dimensional bending beyond the elastic



Figure 1. Dependence of Plastic Endurance Limit N on Cathode Current Density D_{cath} . (a) all specimens exposed to a 3% solution of NaCl and subjected to various maximum stresses as follows: (1) $\delta_{max} = \delta_T$; (2) $\delta_{max} = 1.05 \delta_T$; (3) $\delta_{max} = 1.35 \delta_T$. (b) all specimens subjected to a constant maximum stress $\delta_{max} = 1.05 \delta_T$ during exposure to media of various acidities, as follows: (4) 3% NaCl; (5) 3% NaCl + 0.01 normal H_2SO_4 ; (6) 3% NaCl + 0.1 normal H_2SO_4 ; (7) 3% NaCl + 1 normal H_2SO_4 .

limit (plastic fatigue) with a frequency of 0.8 cps on the IMA IP-1 machine described in [19]. The polarization current was supplied by a storage battery with a spiral platinum anode.

The test results were used to construct "polarization curves", *i.e.*, plots of the plastic endurance limit (cycles to failure N) versus cathode polarization current density (D_{cath}) (Figure 1).

Results and Discussion

As may be seen from Figure 1, all the curves have a similar shape, which permits the conclusion that the processes illustrated by these curves are qualitatively similar. A distinctive feature of these polarization curves is the presence of two maxima (peaks). It is noteworthy that the first maximum always occurs at the same cathode current density (0.0125 A/dm^2) and is independent of both the acid concentration and of the loading stress. The second maximum tends to shift toward the smaller cathode current densities and lower

plastic endurance limits as the latter is lowered by the effect of two factors: an increased loading stress and increased electrolyte acidity. Raising the acid concentration increases the total amount of hydrogen absorbed by the metal, while increasing the loading stress stimulates the diffusion of the hydrogen to the failure zone. Both factors thus have the same result: they increase the local hydrogen concentration in the zone of maximum stresses and shears, thereby accelerating the crack development process.

Since the above-mentioned curves have a similar shape in the case of both neutral (Figure 1a) and acid (Figure 1b) electrolytes, it may be assumed that the failure mechanism is also similar, that is, that hydrogen penetrating the metal from the electrolyte participates in the failure process.

An explanation of these results may be found in the theories on corrosion destruction of metals proposed by V. V. Romanov in [8-10], if we modify his treatment to include the role of hydrogen in these processes. The corrosion current generated at the bottom of different cracks increases with the depth and narrowness of the crack. Therefore, the cathode polarization current will first absorb the corrosion pairs formed by the wider shallower cracks, and then the pairs formed by the narrow deep cracks; that is, as the density of the protective current increases, the number of cracks which form and grow will decrease. When it reaches a certain density, the protective current may completely inhibit all corrosion processes occurring at the surface of the stressed metal. However, in most cases cathode processes are accompanied by corrosion (*i.e.*, anode) processes, with the result that hydrogen is released at the surface which penetrates the metal. Therefore, increasing the cathode current to inhibit corrosion processes at the same time intensifies the absorption of hydrogen by the metal.

As an example of polarization curve analysis we will consider the results of tests in a 3% NaCl solution with $\sigma = \sigma_T$ (Figure 2, curve *a*). Four segments /691 can be distinguished in this curve. Segment I is characterized by a slight increase of the number of cycles to failure which is due to the ordinary effect of cathode protection, that is, to decrease in the intensity of general corrosion. The boundary of segment I for all the curves shown in Figure 1 occurs at a constant value of D_{cath} equal to 0.0125 A/dm^2 . This is obviously related to the properties of the material and does not depend on the test conditions of loading stress and acid concentration. Further increase in the cathode current (segment II) decreases the number of growing cracks, since the growth of small cracks is inhibited and only deep narrow cracks, which have stronger corrosion currents at the bottom, can continue to grow. As the number of growing cracks lessens, stress concentration near the bottom of existing cracks increases (the autodistributing effect of concentrators decreases) [20], shortening the time to failure. At the same time, as the cathode current increases, the process of hydrogen penetration into the metal through microcathode sectors is facilitated. Therefore the total process expressed by the second segment of the curve may be regarded as a process of selective corrosion enhanced by hydrogen absorption, whose effect begins to appear at relatively high current densities in this segment.

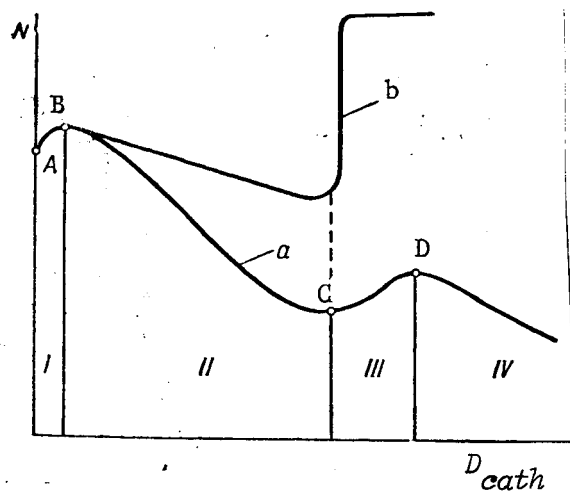


Figure 2. Curve Plotting Cycles to Failure N Versus Cathode Current Density D_{cath} in a Neutral Electrolyte ($\sigma = \sigma_T$). (a) with hydrogen effect; (b) without hydrogen effect (theoretical shape of curve).

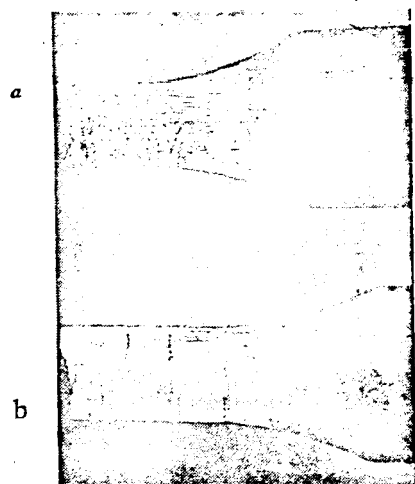


Figure 3. Surface of Specimens After Failure in a 3% NaCl Solution. (a) $D_{cath} = 0.0125 \text{ A/dm}^2$; (b) $D_{cath} = 0.5 \text{ A/dm}^2$.

These hypotheses are confirmed by the character of the surface of the specimens after the test. The surface of a specimen after failure at a current density corresponding to the first maximum (point B, Figure 2) shows a network of corrosion flaws with small cracks radiating from them (Figure 3a). In the sample specimen which failed at a current density corresponding to point C, literally only two or three well-grown cracks are present and no traces of corrosion can be observed (Figure 3b).

In segment III of curve α (Figure 2), current density attains a protective level, *i.e.*, the corrosion processes beginning at point C completely cease to operate. If the process of hydrogen absorption likewise ceased, the curve would assume the shape shown in Figure 2b. The slope of segment II would become less steep, and in segment III the plastic endurance limit would approach the values obtained in air, as was observed in crack tests in which the hydrogen effect did not appear [8-14]. Since in segment III of curve α the hydrogen effect is the determining factor in the failure process, the increase of the plastic endurance limit in this curve is not so striking as in curve b . /692

The observed small increase of the plastic endurance limit in this segment of curve α may be explained as follows. Due to cessation of the selective corrosion effect and the absence of deep stress concentrators, the hydrogen is more uniformly distributed through the specimen. Although the total amount of hydrogen present increases, the severity of the hydrogen effect is lessened, since (in contrast to segment II) the conditions for the concentration of hydrogen in the failure zone become less favorable.

With still further increase in the current density (beginning at point D), the total concentration of hydrogen in the metal becomes the determining factor in the failure process. Because of the monotonic increase of total hydrogen, the endurance of the specimen decreases continuously in segment IV.

Curve 7 (Figure 1b) shows that in tests in electrolytes with a relatively high acid concentration, increasing the cathode current does not sharply reduce the number of cycles.

In this case hydrogen absorption is rather intensive and occurs without cathode polarization; that is, the amount of hydrogen entering into the metal is quite sufficient to produce embrittlement, and increased hydrogen absorption only slightly reduces strength. The same may be said of metal failure at high stress loads (Figure 1, curve 3), when the cumulative effect of plastic deformation builds up so rapidly that neither hydrogen absorption nor corrosion can exert much influence on the failure process.

The shape of the curves obtained will obviously not be the same for all metals. It is determined by many factors associated with the properties of the individual metal, primarily by its tendency to corrosion and hydrogen absorption.

Conclusions

1. Failure under alternating plastic deformation yields polarization curves which are qualitatively similar for conditions of acid and neutral electrolytes with cathode polarization. This indirectly confirms the hydrogen embrittlement of the metal in neutral electrolytes in the presence of plastic fatigue.

2. The decrease in plastic endurance limit under the influence of hydrogen at relatively low cathode current densities is enhanced by the presence of stress concentrators created by selective corrosion.

REFERENCES

1. Karpenko, G. V. and R. I. Kripyakevich: *Vliyaniye vodoroda na mekhanicheskiye svoystva stali.* (The Effect of Hydrogen on the Mechanical Properties of Steel.) Metallurgizdat, 1962.
2. Loginov, A. W. and E. H. Phelps: *Corrosion*, Vol. 16, No. 7, pp. 97-107, 1960.
3. Hughes, T. R., M. Lamborn and G. S. Liebert: *J. of the Iron and Steel Institute*, Vol. 203, No. 2, pp. 183-185, 1965.
4. Truman, J. E., R. Perry and G. N. Chapman: *J. of the Iron and Steel Institute*, Vol. 202, No. 9, pp. 745-756, 1964.
5. Ivanov, S.: *Morskoy Flot*, No. 6, pp. 18-19, 1959.
6. Titov, V. A.: In: *Mezhkristallitnaya korrozziya i korrozziya metallov v napryazhennom sostoyanii.* (Intercrystalline Corrosion and Corrosion of Metals in a Stressed State.) Mashgiz, 1960.
7. Troiano, A. R.: *Corrosion*, Vol. 15, pp. 106-112, 1959.
8. Romanov, V. V.: *Korroziionnoye rastreskivaniye metallov.* (Corrosion Cracking of Metals.) Mashgiz, 1960.
9. Romanov, V. V.: In: *Trudy instituta metallurgii im. Baykova.* (Transactions of the Baykov Institute of Metallurgy.) No. 13, *Metallurgiya, Metallovedeniye, Fiziko-khimicheskiye metody issledovaniya.* (Metallurgy, Metal Science, Physicochemical Research Methods.) Izd-vo AN SSSR, 1962.

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10. Romanov, V. V.: *DAN SSSR*, Vol. 129, No. 4, 1959; *ZhPKh*, Vol. 34, p. 1825, 1961; Vol. 36, p. 2465, 1963.
11. Ryabchenkov, A. V.: *Korroziionno-ustalostnaya prochnost' stali*. (*Corrosion-Fatigue Strength of Steel*.) Mashgiz, 1953.
12. Vvedenkin, S. G. and V. S. Sinyavskiy: *ZhFKh*, Vol. 36, No. 10, 1962.
13. Patrick, D. E. and E. G. Thompson: *J. Amer. Chem. Soc.*, Vol. 75, pp. 1184-1187, 1953.
14. Kripyakevich, R. I., Yu. I. Babey, A. K. Litvin and B. F. Kachmar: In: *Vliyaniye rabochikh sred na svoystva materialov*. (*Influence of Working Media on the Properties of Metals*.) No. 3, Izd-vo "Naukova Dumka", Kiev, 1964, pp. 23-28.
15. Troiano, A. R.: *Spec. Rept. Iron and Steel Inst.*, No. 73, pp. 1-14, 1961.
16. Shkol'nik, L. M.: In: *Korroziionnaya ustalost' metallov*. (*Corrosion Fatigue of Metals*.) L'vov, Izd-vo "Kamenyar", 1964.
17. de Kazinczy, F.: *The Engineers' Digest*, Vol. 17, No. 1, pp. 11-13, 1956; *Jernkontorets Ann.*, Vol. 139, No. 11, pp. 885-892, 1955.
18. Beloglazov, S. M. and M. I. Polukarov: *ZhPKh*, Vol. 33, No. 2, pp. 389-397, 1960.
19. Yankovskiy, L. Ya., V. T. Stepurenko and Yu. I. Babey: In: *Voprosy mashinovedeniya i prochnosti v mashinostroyeni*. (*Problems of Machine Science and Strength in Machine Building*.) No. 8, Izd-vo AN UkrSSR, 1962, p. 77.
20. Karpenko, G. V.: *Prochnost' stali v korroziionnoy srede*. (*Strength of Steel in a Corrosive Medium*.) Mashgiz, 1963.

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